

# Development of Biobased Synthetic Fluids: Application of Molecular Modeling to Structure–Physical Property Relationship<sup>†</sup>

Atanu Adhvaryu,<sup>\*,§</sup> Brajendra K. Sharma,<sup>\*,§</sup> H. S. Hwang,<sup>#</sup> Sevim Z. Erhan,<sup>\*,§</sup> and Joseph M. Perez<sup>‡</sup>

*Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, Food and Industrial Oil Research, U.S. Department of Agriculture (USDA), 1815 North University Street, Peoria Illinois 61604, and Indium Corporation of America, 1676 Lincoln Avenue, Utica, New York 13502*

Biobased synthetic fluids are preferred alternatives to petroleum-based products due to their nontoxic and ecofriendly nature. Recent developments in biobased synthetic lubricants are a result of their comparable performance properties with mineral oils for industrial and automotive applications. These synthetic fluids can be chemically custom designed for a specific application. To develop an optimized molecule that can translate performance properties comparable to or at par with existing petroleum-based products, via chemical synthesis pathway alone, will be an expensive and time-consuming exercise. Molecular modeling of desired compounds and subsequent computation of their minimum energy profile, steric environment, and electron charge density distribution, etc., prior to actual synthesis, can shed valuable information on their physicochemical performance properties. Based on such information, chemical synthesis can be focused only on the promising molecules. Calculations based on equilibrium geometries were optimized using AM1 semiempirical molecular orbital models. It was observed that ring opening of the triacylglycerol epoxy group and subsequent derivatization of the epoxy carbons can improve the oxidation and low-temperature stability of these synthetic lubricant base oils.

## Introduction

Demand for lubricants in the U.S. will reach 2.8 billion gallons in 2006, mainly driven by process oils and high-performance lubricants. The current market share of industrial fluids and lubricants in the U.S. will translate to \$7.6 billion in gross revenue. Most of these products (e.g., engine oils, general industrial oils, transmission and hydraulic fluids, gear oils, and greases) are based on mineral oils. Strict government mandates have encouraged the use of more biobased products and ecofriendly technology. Currently, in the fuel and lubricant sectors there is a significant potential for new product development from renewable resources such as seed oils.<sup>1</sup> The use of seed oil derivatives as lubricant base stocks can reduce our dependence on petroleum crude, widespread use of which continues to pose a threat to the environment and the ecosystem. The amphiphilic nature of the seed oil molecule makes it an excellent candidate as a lubricant and functional fluid.<sup>2,3</sup> For industrial applications, vegetable oil possesses poor thermooxidative, cold flow and hydrolytic stability.<sup>2,3</sup> The hydrolytic instability is due to the ester linkage, while C–C polyunsaturation leads to rapid oxidation, and the presence of saturated long alkyl chains results in cold flow problems. These polyunsaturated sites can be functionalized, leading to a wide range of chemical derivatives with varied properties.

Synthesis of seed oil derivatives followed by product characterization is a lengthy and expensive process. Computer-

generated structural models can guide us to synthesize those derivatives that show promising results. This approach can significantly streamline synthesis efforts to develop new product.<sup>4</sup> Development of a quantitative structure–property relationship using computer-generated models has been successfully applied to predict water solubility<sup>5</sup> and vapor pressure.<sup>6</sup> Efforts were made to translate this approach to understand seed oils' high- and low-temperature behavior. Tan<sup>7</sup> reported the use of molecular orbital indexes to study interaction between lubricant polar end groups and metal surface. In another study, Sundaram<sup>8</sup> demonstrated the use of design-relevant building blocks for a real industrial problem in fuel additive design. Jabberzadeh<sup>9</sup> investigated the effects of branching on rheological properties and behavior of molecularly thin liquid films of alkane in extreme conditions in a thin film lubrication regime. It was observed that dynamics of the molecules and their orientation are affected by the degree of branching. Konno<sup>10</sup> reported evaluation of viscosity employing molecular dynamics simulation and prediction based on neural network, while Yang<sup>11</sup> predicted viscosity, viscosity index, and viscosity pressure coefficients of lubricant size alkanes by applying nonequilibrium molecular dynamics simulations using united atom models for intermolecular interactions. All these studies illustrate the efficiency of computer-generated structural models to help design new lubricants at the molecular level.

The current research is directed toward the elimination of functional drawbacks i.e., oxidation and low-temperature fluidity and improving on the existing properties of seed oil for potential industrial uses. The approach will include computer-generated structural models of seed oil derivatives, calculation of activation energy, understanding the steric environment and molecular symmetry, etc., to help select the right structure for actual synthesis.

\* To whom correspondence should be addressed. Tel.: (309) 681-6532. Fax: 309-681-6340. E-mail: erhansz@ncaur.usda.gov.

<sup>†</sup> Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

<sup>‡</sup> Pennsylvania State University.

<sup>§</sup> USDA.

<sup>#</sup> Indium Corporation of America.

## Experimental Section

Epoxy soybean oil (ESO) was obtained from Elf Atochem North America Inc., Bloomington, MN. The oil (97%+ purity) was used as received from the commercial source without any further purification and processing.

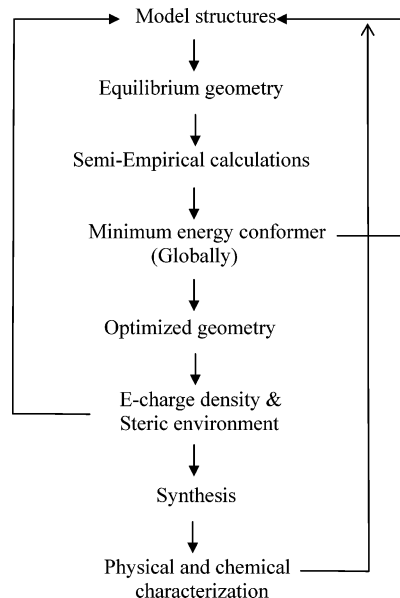
**Molecular Modeling.** Structural models and associated calculations were performed on a PC platform using Spartan Pro software (Wavefunction, Inc., Irvine, CA). Molecular geometries were optimized using AM1 semiempirical orbital models. The calculations are based on a neutral molecule with singlet spin multiplicity. This program also provides for graphical display of parameters resulting from semiempirical molecular orbital and density function calculations, such as electron density and electrostatic potential. These properties can be color-mapped on the molecular surface to illustrate both steric and electrostatic characteristics. Colors represent the electron charge density that is mapped to distinguish electron-rich and electron-deficient regions on the surface of the molecule.

**Synthesis.** The reaction was carried out by heating an alcohol (methanol, 1-hexanol, 2-ethylhexanol) and a catalytic amount of sulfuric acid at 90 °C with stirring. ESO was added, and the mixture continued to stir at 120 °C for 7 h. The reaction mixture was cooled by adding crushed ice and followed by washings with saturated sodium bicarbonate solution. The mixture was extracted with ethyl acetate, dried over anhydrous magnesium sulfate, and filtered and the solvent stripped using a rotary evaporator. Any volatile material including the remaining solvent was removed under vacuum at 80 °C overnight. The corresponding products obtained with the various alcohols are designated as  $\text{CH}_3(\text{CH}_2)_5\text{OH}$ , Syn A;  $\text{CH}_3\text{OH}$ , Syn D, and  $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$ , Syn E.

One of the products Syn A was further reacted with an acid anhydride at 80 °C for 2 h under nitrogen atmosphere. The reaction mixture was cooled with ice water and later extracted with ethyl acetate. The organic layer was washed successively with 5% sodium hydroxide, 5% hydrochloric acid, and 5% sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and filtered and the solvent evaporated with rotary evaporator. Any volatile material including the remaining solvent was removed under vacuum at 80 °C overnight. The corresponding products obtained in this synthesis are  $[(\text{CH}_3)_2\text{CHCO}]_2\text{O}$  designated Syn B and  $[\text{CH}_3(\text{CH}_2)_4\text{CO}]_2\text{O}$  designated Syn C. The synthetic fluids (A through E) were primarily mixtures of different compounds produced during the synthesis process, with the major component being the targeted molecule (90%+ abundance), as determined from NMR analysis (as part of a separate communication).

**Pressurized Differential Scanning Calorimetry.** The equipment used was a PC based pressurized differential scanning calorimetry (PDSC) 2910 thermal analyzer from TA Instruments (New Castle, DE). The pressure module was temperature-calibrated using the melting point of indium metal (156.6 °C) at 10 °C/min heating rate. Typically a 1.5–2.0 mg sample was hermetically sealed in an aluminum pan with a pinhole (open aluminum and steel pans were also used in separate experiments). The sample was oxidized under a static air pressure of 2000 kPa. The system was equilibrated at 50 °C and then ramped at 10 °C/min to an end temperature of 300 °C. The amount of sample in the pan does affect the shape and reproducibility of DSC thermograms. If the sample size is too large, there is a danger of sample sputtering and leaking from the cell. Further, a thin oil film ensures better oil–air interaction.<sup>12,13</sup> The onset temperature of oxidation (OT) for each sample was calculated from the corresponding exotherm. The

**Scheme 1. Computer-Generated Structural Modeling Adopted for the Development of Biobased Synthetic Fluids**



OT is defined as the temperature at which a rapid increase in the rate of oxidation is observed in the system. This temperature is obtained by extrapolating the tangent drawn on the steepest slope of the exotherm to the baseline. The higher the OT, the better the oxidation stability of the oil matrix.

**Thin Film Micro Oxidation.** A 50  $\mu\text{L}$  aliquot of the test oil sample was accurately weighed and placed on a low carbon steel catalyst surface, resulting in a thin oil film. The oil is oxidized under a steady stream of dry gas (20  $\text{cm}^3/\text{min}$ ) in a static reactor maintained at a preset temperature. The experiment can be designed for any combination of temperature (125–275 °C), time (30–180 min), and atmosphere (air, nitrogen, oxygen). A constant gas flow ensures removal of volatile oxidation products while maintaining a steady gas concentration at the oil surface. The test method was designed to eliminate any oxygen diffusion limitations. In this procedure, the oil samples were oxidized in air at different temperatures (150–250 °C) for a period of 2 h. Upon completion of test time, the catalyst containing the oxidized oil sample was removed, rapidly cooled under a steady flow of dry  $\text{N}_2$ , and transferred to a desiccator for temperature equilibration. The catalyst containing the oxidized oil was then weighed to determine volatile loss (or gain) due to oxidation and then soaked (30 min) in tetrahydrofuran (THF) to dissolve the soluble portion of the oxidized oil. After dissolving the soluble portion, the catalyst was dried and finally weighed to determine the remaining oil-insoluble deposit. The THF-soluble fraction may be separately analyzed for molecular weight distribution by gel permeation chromatography, functional group identification by infrared, or structure elucidation by nuclear magnetic resonance spectroscopy.

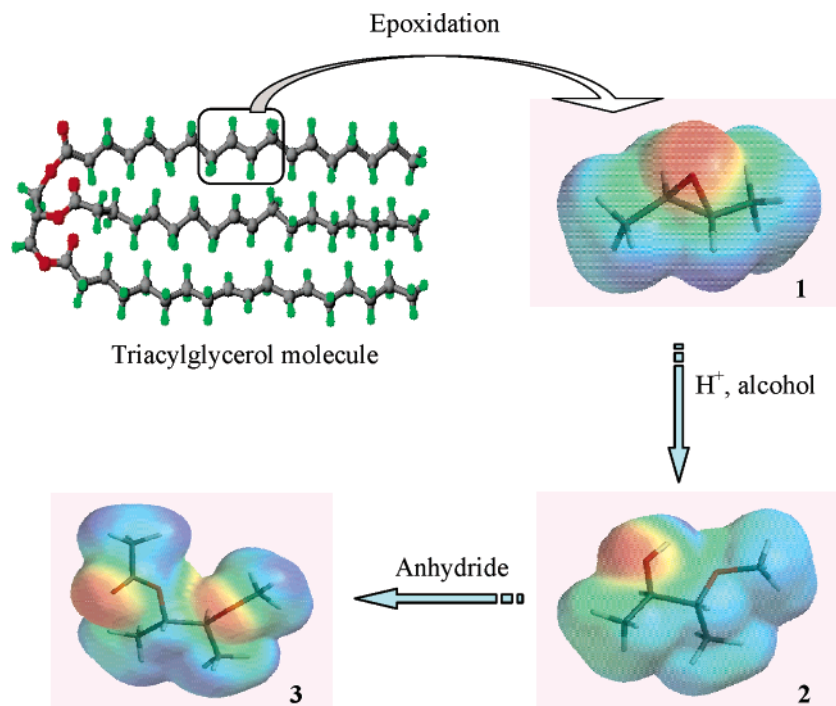
## Results and Discussion

**Designing Model Systems and Energy Minimization Approach.** Computer-generated structural modeling of a representative molecule and subsequent computation of equilibrium energy are often helpful information prior to actual synthesis. In most cases, knowledge of calculated energy, electron charge distribution, steric environment, and structure–property correlations can guide synthesis efforts. Scheme 1 presents the process flow adopted in the current study. Semiempirical

**Table 1. Calculated Minimum Energy and Experimental Physical Property Data<sup>a</sup> of Synthetic Oils<sup>b</sup>**

compd designation	$E_{\min}$ (kcal/mol)	OT <sup>c</sup> (°C)	OT <sup>d</sup> (°C)	OT <sup>e</sup> (°C)	insoluble deposit <sup>f</sup> (wt %)	pour point <sup>g</sup> (°C)	KV <sup>h</sup> at 40 °C, cSt	KV <sup>h</sup> at 100 °C, cSt	VI <sup>i</sup>
1, epoxy	8.93	195.5	217.4	203.8	70	3	170		
2, OH ether	27.48								
3, ester ether	16.42								
Syn A	23.87	221.1	246.1	152.4	36	0	viscous		
Syn B	14.42	190.6	228.3	188.3	43	-6	225	26.3	150
Syn C	9.92	230.6	236.8	200.8	30	-9	207	24.8	150
Syn D	13.58	151.0	159.4	166.4	10	3	41.2	5.9	78
Syn E	16.30	159.4	198.0	179.2	44	-18	53.4	8.1	121

<sup>a</sup> DSC data reported are the average value of three independent experiments; repeatability of the data,  $\pm 0.8$ . <sup>b</sup> Synthetic fluids A–E are mixtures with a 90%+ abundance of the target molecule. <sup>c</sup> PDSC data with pinhole hermetic aluminum pan. <sup>d</sup> PDSC data with open aluminum pan. <sup>e</sup> PDSC data with open steel pan. <sup>f</sup> Microoxidation, 2 h, 200 °C; average of two experiments; repeatability of the data,  $\pm 1.2\%$ . <sup>g</sup> ASTM D 97. <sup>h</sup> Kinematic viscosity using ASTM D 445. <sup>i</sup> Viscosity index using ASTM D 2270.

**Figure 1.** Computer-generated molecular structures: epoxy (1), hydroxyl ether (2), and ester ether (3).

models follow directly from Hartree–Fock models. Here the entire molecule is treated with respect to its valence electrons.<sup>14,15</sup> This model is particularly useful where the equilibrium structure, in its minimum energy conformation, involves a large molecule. Since thermochemical properties are largely based on electron density distribution, it is always necessary to utilize the exact equilibrium geometry of the target molecule.

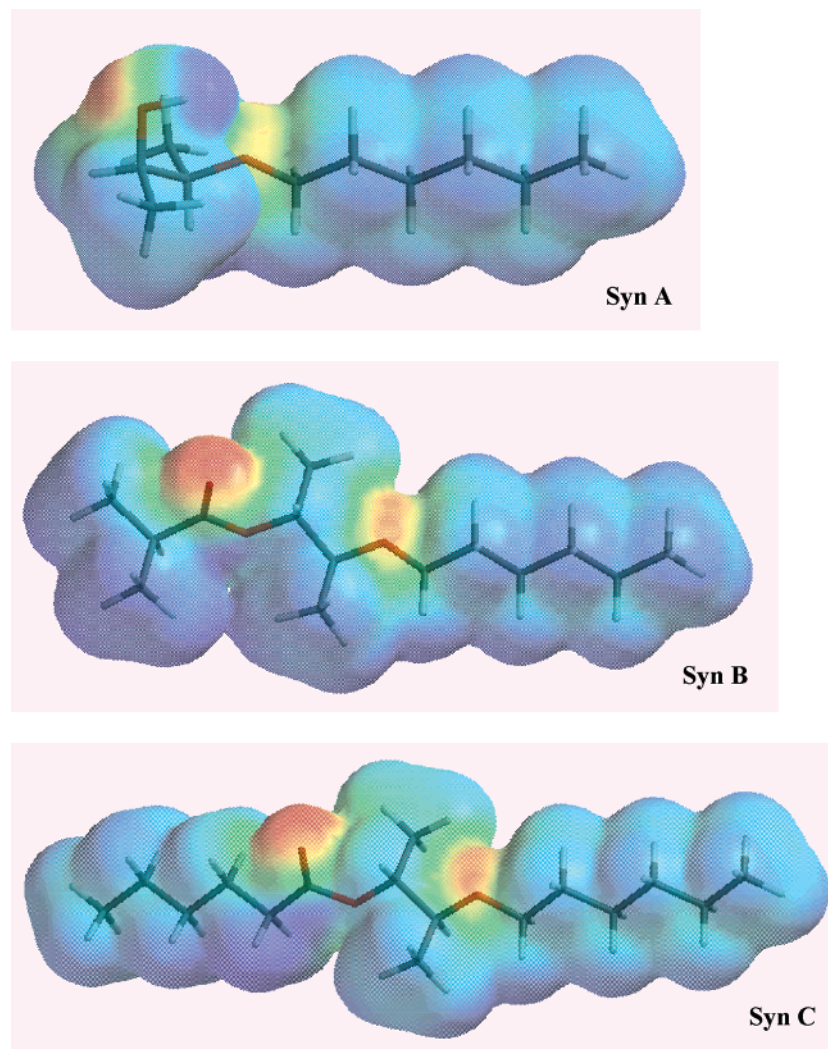
**Chemical Modification Based on Energy Calculations.** Seed oils are primarily composed of triacylglycerol (TG) molecules. The ester chains are derived from fatty acids (FA), typically stearic (C<sub>18:0</sub>), oleic (C<sub>18:1</sub>), linoleic (C<sub>18:2</sub>), and linolenic (C<sub>18:3</sub>) [numbers in the subscripts indicate an 18-carbon chain with 0, 1, 2, or 3 unsaturated sites, respectively]. Polyunsaturation in the FA chains leads to poor oxidation stability, whereas complete saturation of the double bonds results in poor low-temperature fluidity. Therefore, a limiting situation is reached beyond which further improvement in high- and low-temperature stability cannot be attained. This inherent drawback in TG molecules limits their use in industrial applications operating under a broad temperature range. Chemical modification of TG will help build molecules with desirable properties for lubricant applications, as all the physical and chemical properties of seed oil are solely based on the molecular structure and their relative distribution. This approach holds a lot of potential in designing new molecules, including those not yet

synthesized. It is also a screening tool to identify the appropriate structure for a specific application.

Epoxidation reaction improves the oxidation stability of the TG molecule by eliminating C–C polyunsaturation in the fatty acid chain. Three-dimensional orientations of the TG molecule with different fatty acid (oleic, linoleic, and linolenic) chains are different. In an oleic acid chain, the two -CH<sub>2</sub>- planes adjacent to the C–C double bond are oriented in different planes creating an angle. Linoleic chain (two C=C bonds separated by bisallylic hydrogens) results in -CH<sub>2</sub>- planes that are in staggered orientation, thus increasing the overall steric bulk in the chain when viewed along the chain length. The distance between the two hydrogens on the same FA chain of linoleic and oleic acids are 13.73 and 11.40 Å, respectively. The linoleic chain would therefore have greater steric bulk compared to an oleic chain. Epoxidation restores uniformity in the chain and therefore offers low steric hindrance during the cooling process. Such molecules would readily undergo crystallization (the pour point of soybean oil and epoxidized soy oil is -6 and 3 °C, respectively).

The minimum energy ( $E_{\min}$ ) of the epoxy structure, 1, is 8.93 kcal/mol (Table 1). The electron density plot is shown in Figure 1. The molecule is thermally stable up to a moderate temperature range<sup>16</sup> compared to TG. However, when exposed to higher temperature over extended time, epoxy oils undergo rapid





**Figure 2.** Simplified electron density models for synthetic oils A–C.

oxidative degradation. Epoxy ring opening with acid catalysis (perchloric or sulfuric acid) and a suitable alcohol (ROH) would result in a hydroxyl ether compound, **2**. The  $E_{\min}$  for **2** in trans-conformation is 27.48 kcal/mol and is significantly higher than that for **1**. The increase is due to steric interaction from oxygen lone pairs ( $\ddot{O}$ ) of hydroxyl and ether groups. Due to the presence of free -OH groups in **2**, the fluid is highly viscous as a result of H-bonding. Further reaction with an anhydride resulted in an ester ether compound, **3** ( $E_{\min} = 16.42$  kcal/mol). The addition of a carbonyl group at -OH displaces the electron cloud toward the more electronegative C=O group. The overall steric interaction from  $\ddot{O}$  is lowered in this case. The electron potential map on **3** (Figure 1) clearly shows that the electron-deficient H sites are more distributed in the molecule (near the -COCH<sub>3</sub> hydrogens) when compared to **2**, where the sole electron-deficient H was directly attached to O. This labile H on **2** is highly susceptible to deprotonation under oxidizing conditions.

In a large molecule (e.g., TG), such a chemical transformation can bring about a dramatic change in thermooxidative and low-temperature behavior. On the basis of our experience with energy calculations and structure–property relationships in compounds **1–3**, we could make a generalized prediction for chemically modified derivatives of TG molecule (Syn A–E). Figure 2 presents the optimized minimum energy geometry of the molecules representing synthetic fluid A–C. The figures depict only the branched carbon sites, and the long FA chain in the molecule has been truncated to offer clarity. Synthetic

fluid A has a residual hydroxyl group that was separately functionalized with a short-branched chain (yielding Syn B) and long chain (yielding Syn C) molecule.

An electron charge density map shows a labile hydrogen atom in Syn A that can be easily protonated. There is significant steric interaction with the oxygen lone-pair electron cloud ( $E_{\min} = 23.87$  kcal/mol; Table 1). The -OH group can participate in H-bonding and consequently increase the fluid viscosity. After conversion to Syn B, the distance between the  $\ddot{O}$  lone pair electron cloud can be increased. There is however a residual instability in Syn B ( $E_{\min} = 14.42$  kcal/mol) from adjacent C=O and Me steric interaction. Incorporation of a long-chain substitution in Syn A can release the bulk strain in the molecule and also improve the low-temperature fluidity and viscosity characteristics of the fluid, resulting in Syn C ( $E_{\min} = 9.92$  kcal/mol). Synthetic routes for the Syn A–C is shown in Scheme 2. Realistically it is quite a challenge to improve both oxidation and low-temperature properties using the same chemical modification. In most cases improving one property destroys the other. Therefore it is very important to design an optimized structure that will offer the best performance properties over a broad spectrum.

This fact is illustrated in Figure 3 for synthetic fluids D and E (the FA chains in the figures are truncated for clarity). The molecules were designed to illustrate the effect of chain length and branching on their minimum energy and further translate that to predict their physical and chemical properties. Scheme

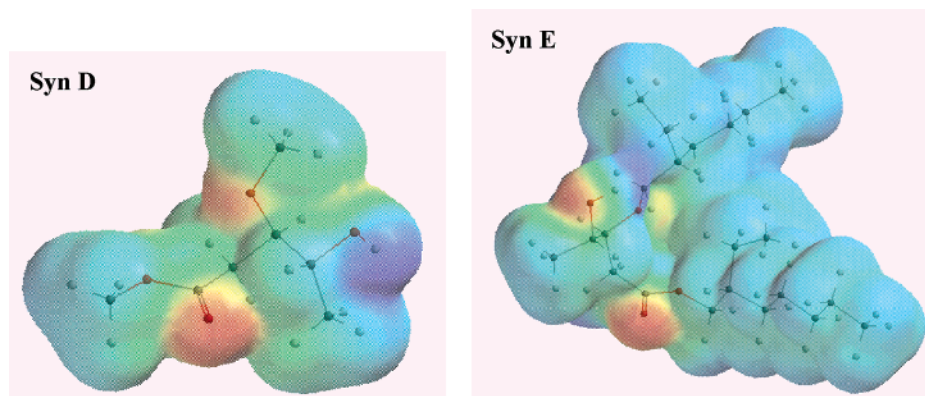
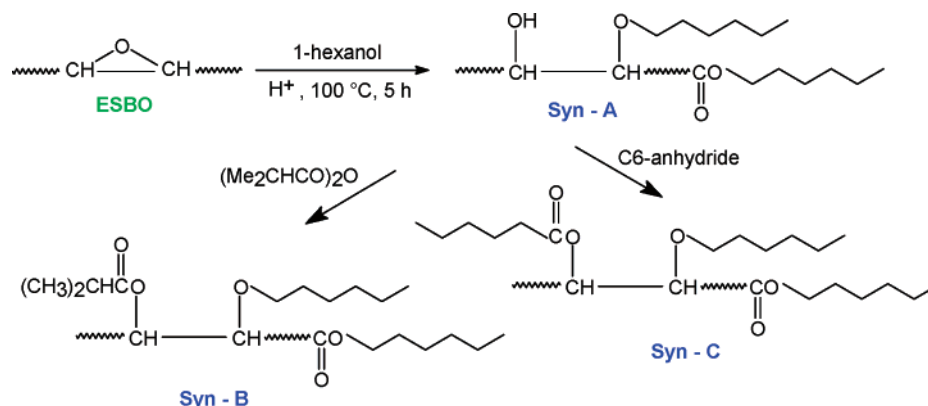
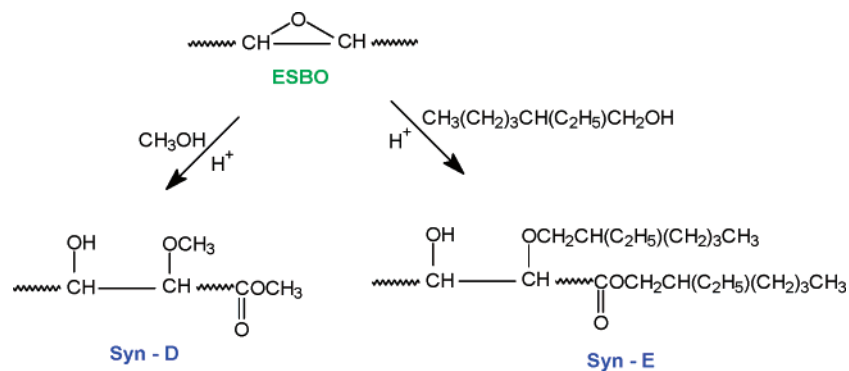


Figure 3. Simplified electron density models for synthetic oils D and E.

**Scheme 2. Reaction Path for Synthetic Fluids A–C**



**Scheme 3. Reaction Path for Synthetic Fluids D and E**



3 presents the synthetic routes to prepare Syn D and E. Short-chain substitution in Syn D resulted in a higher pour point, whereas a bulky and asymmetrically branched chain will prevent microcrystal formation during the cooling process in Syn E, thus delaying solidification.<sup>17</sup> Substitution of a bulkier and branched alcohol (2-ethylhexanol) in Syn E shows a significant lowering in the pour point ( $-18\text{ }^{\circ}\text{C}$ ) compared to methanol in Syn D ( $3\text{ }^{\circ}\text{C}$ ). The  $E_{\min}$  for the bulkier molecule (Syn E) is 16.3 kcal/mol compared to 13.6 kcal/mol for Syn D. This factor will also contribute to low oxidation stability in Syn E (Table 1).

**Analysis of PSDC Data and Molecular Structure.** PSDC is an accelerated oxidation method and has been applied quite extensively for the evaluation of thermooxidative behavior of vegetable and mineral oils.<sup>18–21</sup> Typically test samples in a pinhole aluminum pan gave a lower OT compared to an open pan (Table 1). Removal of volatile organic compounds (VOCs) formed during the initial phase of oxidation in pinhole pans are largely restricted within the pan volume and close to the

metal surface. Oxidation in the vapor phase is more rapid than the liquid phase, therefore shortening the OT. Further, the rate of diffusion of air into the pinhole capsule is much faster compared to high molecular weight VOCs (diffusing out of the capsule), resulting in an accumulation of volatile products of oxidation within the capsule. This is clearly not the situation in open pans where low molecular weight VOCs are continuously lost from the metal surface to the surrounding gas phase. It was also observed that the oils are more reactive on a steel surface than on aluminum, which can trigger an early OT. The increase in reactivity results in lowering OT. Free hydroxyl groups of synthetic oil A, D, and E makes strong chemical interaction with the more reactive steel surface. This interaction is as a result of iron atoms being able to offer coordination sites to polar oxygen atoms (making the vacant outer d-orbital of the transition metal available for the oxygen lone pairs).

$E_{\min}$  values for Syn A–C are influenced by substitution, steric interaction, and distribution of electronic charge density in the

molecule. Using the more reactive steel surface in DSC, there is a progressive increase in the OT as the free -OH group is substituted with  $-\text{COCH}(\text{CH}_3)_2$  in Syn B and  $-\text{CO}(\text{CH}_2)_4\text{CH}_3$  in Syn C. Steric hindrance from  $\ddot{\text{O}}$  is similar and relatively higher in Syn D and E as compared to Syn B and C. This fact is supported from the DSC data using steel pans.

**Molecular Structure and Thermooxidative Stability Determined Using TFMO.** Oxidation is the single most important reaction of oil resulting in increased acidity, corrosion, viscosity, volatility, and deposit, among others. A thin-film microoxidation test can be conveniently designed to simulate conditions that closely resemble industrial applications. The test yields useful information on evaporation, deposit, additive response behavior, and kinetics of oxidation.<sup>16,22</sup> During the oxidation process, the base fluid undergoes reaction with atmospheric oxygen to form primary oxidation products, which in the presence of metal catalyst undergoes further oxidative polymerization, leading to oil-insoluble deposits. The rate of deposit formation with time and temperature variation gives a good indication of the test fluid stability. It was observed that the deposit remained fairly low for all the fluids Syn A–E at temperatures lower than 175 °C (data not reported). At 200 °C Syn D showed the lowest deposit followed by others (Table 1). The relatively large difference in the percent deposit for Syn D and E is as a result of steric bulk in the latter. This is also reflected from their  $E_{\text{min}}$  (Syn D, 13.58 kcal/mol; Syn E, 16.30 kcal/mol). Synthetic oils A and B have a higher deposit compared to Syn C. The relatively low deposit resulting from oxidation of Syn C can also be explained from its  $E_{\text{min}}$  value.

## Conclusions

Development of a suitable molecule of lubricant via chemical synthetic pathway alone will be expensive and a lengthy process. Computer-based structural models, analysis of equilibrium energy, electron density distribution, and spatial orientation of the functional groups can reflect on important properties such as oxidation, molecular reactivity, low-temperature fluidity, viscosity, and lubricity, etc. Minimum energy calculations using semiempirical geometry of the molecule can be used to generate an electrostatic potential map and steric environment of the molecule. It has been shown in this study that these parameters can be used to explain important properties of the targeted synthetic base oil molecule such as oxidation, high-temperature deposit formation, low-temperature fluidity, and viscosity–temperature characteristics.

On the basis of the minimum energy profile and the charge distribution around the labile hydrogen or a functional group in the molecule, chemical reactivity can be predicted. It was observed that ring opening of the epoxy group and subsequent derivatization of the epoxy carbons can improve the oxidative and low-temperature stability of the molecule. The presence of the hydroxyl group in the molecule also increased the viscosity through intermolecular H-bonding.

Modeling triacylglycerols and their derivatives in an effort to develop synthetic fluids is difficult mainly because of the high molecular weight of vegetable oil molecules and variations in the fatty acid chain structures. To arrive at the minimum energy conformation for such a molecule is difficult and often involves lengthy iterations (Scheme 1). The software limits simultaneous energy minimization of multiple molecules and their effect on each other. However, the approach presented here clearly illustrates that the data from molecular modeling can

predict important properties of biobased derivatives and therefore focus our efforts on selective synthesis.

## Literature Cited

- (1) Stempfel, E. M. Practical experience with highly biodegradable lubricants, especially hydraulic oils and lubricating greases. *NLGI Spokesman* **1998**, 62 (1), 8–23.
- (2) Zaher, F. A.; Nomany, H. M. Vegetable oils and lubricants. *Grasas Aceites (Seville)* **1988**, 39, 235–238.
- (3) Willing, A. Lubricants based on renewable resources—An environmentally compatible alternative to mineral oil products. *Chemosphere* **2001**, 43, 89–98.
- (4) Camarda, K. V.; Sunderesan, P.; Siddhaye, S.; Suppes, G. J.; Heppert, J. An Optimization Approach to the Design of Value-Added Soybean Oil Products. *European Symposium on Computer Aided Process Engineering—11*; Gani, R., Jorgensen, S. B., Ed.; Elsevier Science B. V.: Amsterdam, 2001; pp 369–374.
- (5) Liang, C.; Gallagher, D. A. Prediction of physical and chemical properties by quantitative structure–Property relationships. *Am. Lab.* **1997**, 29, 34–40.
- (6) Liang, C.; Gallagher, D. A. QSPR prediction of vapor pressure from solely theoretically derived descriptors. *J. Chem. Inf. Comput. Sci.* **1998**, 38, 321–324.
- (7) Tan, Y.; Huang, W.; Wang, X. Molecular orbital indexes criteria for friction modifiers in boundary lubrication. *Tribol. Int.* **2002**, 35, 381–384.
- (8) Sundaram, A.; Venkatasubramanian, V.; Caruthers, J. M. In *Computer Aided Molecular Design: Theory and Practice*; Achenie, L. E. K., Gani, R., Venkatasubramanian, V., Eds.; Elsevier Science B. V.: Amsterdam, 2003; pp 329–353.
- (9) Jabbarzadeh, A.; Atkinson, J. D.; Tanner, R. I. The effect of branching on slip and rheological properties of lubricants in molecular dynamics simulation of Couette shear flow. *Tribol. Int.* **2002**, 35, 35–46.
- (10) Konno, K.; Kamei, D.; Yokosuka, T.; Takami, S.; Kubo, M.; Miyamoto, A. The development of computational chemistry approach to predict the viscosity of lubricants. *Tribol. Int.* **2003**, 36, 455–458.
- (11) Yang, Y.; Pakkanen, T. A.; Rowley, R. L. NEMD simulations of viscosity and viscosity index for lubricant-size model molecules. *Int. J. Thermophys.* **2002**, 23 (6), 1441–1454.
- (12) Placek D. G.; Shankwalkar, S. G. Flammability limits of synthetic lubricant base stocks as measured by a modified oxygen index test. *Lubr. Eng.* **1993**, 49 (5), 415–417.
- (13) Adhvaryu, A.; Perez, J. M.; Singh, I. D. Application of quantitative NMR spectroscopy to oxidation kinetics of base oils using a pressurized differential scanning calorimetry technique. *Energy Fuels* **1999**, 13, 493–498.
- (14) Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1986.
- (15) Stewart, J. J. P. Reviews of semiempirical methods. *J. Comput.-Aided Mol. Des.* **1990**, 4, 1.
- (16) Adhvaryu, A.; Erhan, S. Z. Epoxidized soybean oil as a potential source of high-temperature lubricants. *Ind. Crops Prod.* **2002**, 15 (3), 247–254.
- (17) Adhvaryu, A.; Erhan, S. Z.; Perez, J. M. Wax appearance temperatures of vegetable oils determined by differential scanning calorimetry: Effect of triacylglycerol structure and its modification. *Thermochim. Acta* **2003**, 395 (1–2), 191–200.
- (18) Kowalski, B. Determination of oxidative stability of edible vegetable oils by pressure differential scanning calorimetry. *Thermochim. Acta* **1989**, 156, 347.
- (19) Kowalski, B. Thermal-oxidative decomposition of edible oils and fats. DSC studies. *Thermochim. Acta* **1991**, 184, 49.
- (20) Kowalski, B. Evaluation of activities of antioxidants in rapeseed oil matrix by pressure differential scanning calorimetry. *Thermochim. Acta* **1993**, 213, 135.
- (21) Sharma, B. K.; Stipanovic, A. J. Development of a new oxidation stability test method for lubricating oils using high-pressure differential scanning Calorimetry. *Thermochim. Acta* **2003**, 402, 1–18.
- (22) Adhvaryu, A.; Erhan, S. Z.; Sahoo, S. K.; Singh, I. D. Thermo-oxidative stability studies on some new generation API Group II and III base oils. *Fuel* **2002**, 81 (6), 785–791.

Received for review August 8, 2005

Revised manuscript received November 10, 2005

Accepted November 29, 2005